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# 論 文 の 要 旨

題 目　High-performance organosilica membranes for separation of organic solvent mixtures in reverse osmosis and pervaporation
(逆浸透および浸透気化による有機溶媒分離のための高性能オルガノシリカ膜)

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As a proof-of-concept, the research interest of this thesis is mainly focused on organic solvent reverse osmosis separation (OSRO) through organosilica membranes, and pervaporation separation of organic liquids is also included. First, starting with a bridged organosilica membrane derived from BTESA, the viability of organosilica membrane for OSRO was demonstrated by high-pressure reverse osmosis separation of multiple organic azeotropes. Besides, it was found that the permeation behavior of organic liquids through different organosilica membranes in the OSRO modality could be successfully described by a generalized solution-diffusion model. On the other hand, the pervaporation separation performance of organosilica membranes for organic liquids was investigated by a theoretical and experimental study, and was compared with that by OSRO.

The main conclusions in this thesis were summarized as follows:

(1): We pioneered a strategy for the reverse osmosis separation of organic solvents, and used theoretical calculation to confirm extreme energy-savings relative to the conventional methods of distillation and pervaporation. The as-prepared BTESA membranes displayed excellent methanol-selective separations of toluene, methyl acetate, DMC, and MTBE, which can be attributed to the characteristics of size and/or shape sieving. The BTESA membranes used in OSRO outperformed the results of conventional methanol/toluene separations in pervaporation that requires much more energy. Most importantly, no obvious degradation in membrane performance occurred during a long-term measurement under an organic environment for almost 60 days, and the BTESA membranes demonstrated a high level of mechanical strength by enduring a transmembrane pressure of up to 18 MPa. These findings provide novel and drastic innovations for the use of OSRO.

(2): We proposed organosilica as a material platform for organic solvent reverse

osmosis (OSRO), and three different organosilica-derived membranes (BTESA, F-BTESM and CTAC-BTMSH) were prepared for the OSRO separation of methanol/toluene. All of the membranes were highly methanol-selective, and the optimal separation performance was achieved with the BTESA membrane, which gave the highest values for both permeation flux and rejection. Meanwhile, the stable nature of organosilica membranes was also confirmed via a long-term monitoring for 60-90 days. Subsequently, the scope of BTESA membranes was further extended by the challenge of separating methanol/methyl acetate, methanol/DMC, and methanol/MTBE azeotropes across wide ranges of pressures (6-14 MPa) and feed concentrations (0-55 wt%). The BTESA membranes were able to discriminate between molecules with nearly identical molecular weights based on their different shapes. Most importantly, the separation behavior of organosilica membranes under OSRO was accurately predicted using a generalized solution-diffusion model. The predictions described well the resultant pressure-dependent experimental flux and rejection irrespective of membrane types and feed compositions. These findings are expected to be beneficial in the early development of OSRO technology.

(3): This study is the first documentation of the pervaporation performance of organosilica-based membranes for organic/organic systems. Ultrathin and defect-free BTESA membranes were successfully prepared at 300 ºC on tubular α-$Al_2O_3$ supports. This study confirmed the reliable reproducibility and superior chemical tolerance of BTESA membranes via single-gas permeation measurement and in the pervaporation separation of all concentrations of methanol/DMC mixtures as well as by a long-term test for 90 days. The preferential sorption of methanol and the efficient size-sieving of DMC by BTESA membranes led to an ultrahigh separation factor of approximately 120 for a 10 wt%/90 wt% methanol/DMC mixture at 50 ºC, and showed a permeation flux of 2~4 kg $m^{-2}$ $h^{-1}$. In addition, the pervaporation performance of BTESA membranes was well characterized by a generalized solution-diffusion model, and was further proven during the pervaporation of additional methanol/methyl acetate and methanol/MTBE mixtures. The as-prepared BTESA membranes enabled the rapid and efficient removal of methanol from methanol/organic azeotropes.